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ASAHI CHEM IND CO LTD (ASAH)

CLAIMS

(57) [Claim(s)]

[Claim 1] $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$ (a kind is expressed M expresses a kind, even if there are few transition metals, and even if there are few non-transition metals, N) x, and y and z are the number of each $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, and $0 \leq z \leq 0.10$, and the value of y shows the total value, when using two or more sorts of transition metals. The nonaqueous rechargeable battery which considers as a positive-electrode main active material, uses a lithium and a copper multiple oxide as a positive-electrode secondary active material, and uses as a negative electrode the matter which can intercalate a lithium ion.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[Industrial Application]

This invention relates to the rechargeable battery excellent in especially the overdischarge property about a new rechargeable battery.

[Description of the Prior Art]

Nonaqueous rechargeable batteries being a high voltage and a high energy consistency compared with a water-solution system cell, and excelling before in self-discharge etc. is expected very much. The high electromotive force beyond 3V is acquired, and extremely, energy density is high and, especially as for the nonaqueous rechargeable battery which uses as positive active material the lithium currently indicated by JP,55-13613,A, JP,62-90863,A, JP,63-299056,A, etc., and transition metals and the multiple oxide which will consist of non-transition metals etc. if it requires further, it is expected very much as a next-generation high performance rechargeable battery. Furthermore, even if the lithium multiple oxide itself has already contained the lithium as ion and it does not necessarily use a metal lithium as a negative-electrode active material as a description at the time of using this multiple oxide as a positive electrode, it also has the description that a fuel cell subsystem can be formed, and it is expected also as a cell excellent also in the field of safety.

[Problem(s) to be Solved by the Invention]

Thus, it can be said to be the rechargeable battery which may have a lithium, transition metals, and the property excellent in the cell which used the multiple oxide with non-transition metals for the positive electrode when requiring further.

Usually, even if it carries out overdischarge in the case of the nickel-cadmium battery or lead accumulator which is a native water-solution system rechargeable battery, there is no ***** problem.

On the other hand, if overdischarge is carried out to 0V, however it may charge in the case of a nonaqueous rechargeable battery, it does not return to the condition of a basis. As this reason, it thinks as follows.

Either the capacity of a positive electrode or the capacity of a negative electrode is exhausted previously, potential is reduced to a partner's discharge potential, or discharging until an electrical potential difference is set to 0V can pull up, and the electrical potential difference as the whole cell is set to 0V. When considering the case

where the capacity of a positive electrode is exhausted previously first discharge is completed, the potential of a positive electrode will be reduced to the potential of a negative electrode. Although ***** is about 1V, if it becomes below the potential to a lithium, even if the inorganic compound generally used as positive active material of a nonaqueous rechargeable battery will cause change to the crystal structure and will charge it again, it stops returning to a basis below a certain potential.

Next, considering the case where the capacity of a negative electrode is exhausted previously, the potential of a negative electrode can be pulled up to the discharge potential of a positive electrode. In this case, although it changes with classes of positive electrode to be used, depending on more than 3V and the case, it can pull up to about 4V to a lithium. In this case, ingredients, such as a negative-electrode charge collector, can material, and lead tab material, will dissolve electrochemically not to mention degradation of a negative-electrode active material. Although that discharge potential is high when the lithium multiple oxide especially expressed with the above-mentioned general formula $\text{Li}_x\text{MyNzO}_2$ is used as a positive electrode therefore, it is influenced [this] remarkably. Furthermore, it is also possible to use the matter which the fuel cell subsystem using this lithium multiple oxide as a positive electrode can be assembled in the state of the condition which contained the lithium ion like the above-mentioned at the time of the assembly, i.e., discharge, can deposit a lithium metal in a negative electrode by the initial charge, and can be used as a negative-electrode active material, or can carry out the in hawk rate of the cations, such as a conductive polymer and a carbonaceous ingredient, by the initial charge as other combination, and this serves as a big advantage. therefore, when especially a lithium multiple oxide is used as a positive electrode, the difference of the value of the current efficiency at the time of each initial charge of a positive electrode and a negative-electrode active material will determine a positive electrode and the charge capacity of each negative electrode. Generally, a lithium multiple oxide shows about [the current efficiency] 100% of value at the time of an initial charge, and a usual state is larger than the value of the current efficiency of a negative electrode. this -- this fuel cell subsystem -- negative-electrode capacity -- a rate-limiting charge-and-discharge cycle will be repeated. It means that the potential of a negative electrode can pull up this fact even to the discharge potential of a positive electrode again when the aforementioned overdischarge condition, i.e., cell voltage, is set to 0V. That is, degradation of the cell engine performance will be caused in the case where the latter of said case, i.e., the capacity of a negative electrode, is exhausted previously.

Therefore, this lithium multiple oxide can be used in the state of overdischarge like [the cell using positive active material] other nonaqueous rechargeable batteries, and it becomes the big constraint in the case of cell use.

This invention aims at amelioration of the overdischarge property of a cell of having used this lithium multiple oxide as positive active material.

[The means for solving a technical problem]

In order to solve the above-mentioned trouble, this invention is $\text{Li}_x\text{MyNzO}_2$ (a kind is expressed even if there are few transition metals, M). a kind is expressed at least, x, and y and z are the number of each $0.05 \leq x \leq 1.10$, $0.85 \leq y \leq 1.00$, and $0 \leq z \leq 0.10$, and N shows the total value, when [of non-transition metals] the value of y uses two or more sorts of transition metals. Let the nonaqueous rechargeable battery which considers as a

positive-electrode main active material, uses a lithium and a copper multiple oxide as a positive-electrode secondary active material, and uses as a negative electrode the matter which can intercalate a lithium ion be an offer plug.

[For **]

Although either capacity of a positive electrode and a negative electrode will be exhausted previously when overdischarge of the cell is carried out to 0V like the above-mentioned, if nothing copes with it for the aforementioned reason when a lithium multiple oxide is used as positive active material, the capacity of a negative electrode will be exhausted previously, and the aforementioned problem will be caused.

This is produced from imbalance with the amount of intercalation compound formation of the lithium ion burst size by the positive-electrode anode reaction of the lithium multiple oxide at the time of an initial charge, and the conductive polymer by the negative-electrode cathode reaction of this lithium ion and a carbonaceous ingredient like the above.

In order to cancel this imbalance, it can consider making a lithium ion emit also from subactive materials other than a lithium multiple oxide at the time of an initial charge. When the subactive material itself emits a lithium ion, even if it does not have discharge potential or has discharge potential as a property required of this subactive material, what has the potential not more than 2.7V preferably below 3V to a lithium is desirable.

this invention persons have a lithium and a copper multiple oxide very useful about various matter as this positive-electrode secondary active material wholeheartedly as a result of examination, and found out bringing about very remarkable effectiveness.

In the lithium multiple oxide shown by the general formula $\text{Li}_x\text{M}_y\text{N}_z\text{O}_2$ used as a positive-electrode main active material by this invention, M expresses a kind that there are few transition metals, and N expresses a kind that there are few non-transition metals. Although especially M is not limited, if the example is shown, Co, nickel, Fe, Mn, V, Mo, etc. are mentioned, and although especially N similarly is not limited, aluminum, In, Sn, etc. will be mentioned. The condition which contained Li ion for the concrete example, If the chemical formula in a discharge condition shows, namely, LiCoO_2 , LiNiO_2 , $\text{LiCo}_{0.97}\text{Sn}_{0.03}\text{O}_2$, $\text{LiCo}_{0.96}\text{aluminum}_{0.05}\text{O}_2$, $\text{LiCo}_{0.98}\text{In}_{0.06}\text{O}_2$, $\text{LiCo}_{0.75}\text{nickel}_{0.23}\text{O}_2$, $\text{LiCo}_{0.85}\text{Fe}_{0.10}\text{O}_2$, $\text{LiCo}_{0.80}\text{nickel}_{0.17}\text{Sn}_{0.02}\text{O}_2$, $\text{LiCo}_{0.85}\text{Fe}_{0.10}\text{Sn}_{0.05}\text{O}_2$, $\text{LiCo}_{0.85}\text{Mn}_{0.15}\text{O}_2$, $\text{LiCo}_{0.85}\text{V}_{0.11}\text{O}_2$, and $\text{LiCo}_{0.83}\text{Mo}_{0.15}\text{O}_2$ grade are mentioned.

Moreover, the value of x is changed according to a charge condition and a discharge condition, and the range is $0.05 \leq x \leq 1.10$. That is, DIN TAKARESHON of a lithium ion happens by charge, the value of x becomes small, and the value of x amounts to 0.05 in a full charge condition. Moreover, the intercalation of a lithium ion happens by discharge, the value of x becomes large, and the value of x amounts to 1.10 in a full discharge condition.

Moreover, the value of y does not show the total value, when using two or more sorts of transition metals, the value of y is not changed by charge and discharge, but the range of it is $0.85 \leq y \leq 1.00$. When the value of y exceeds less than 0.85 and 1.00, phenomena, such as a fall of cycle nature and a rise of an overvoltage, occur, engine performance sufficient as an active material for rechargeable batteries is not obtained, and it is not desirable.

Moreover, it is the range of $0 \leq z \leq 0.10$, and the basic property as an active material for

rechargeable batteries is spoiled, and the value of z is not desirable, when the value of z exceeds 0.10.

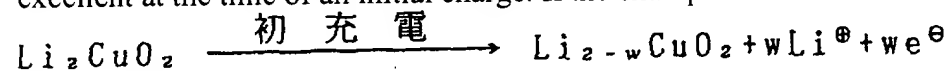
This $\text{Li}_x\text{MyN}_z\text{O}_2$ can be obtained by well-known approach which is in JP,62-90863,A etc. that is, after making Li, M, the oxide of the metal of each N, a hydroxide, a carbonate, a nitrate, an organic-acid salt, etc. mix, it is obtained by calcinating 600-950 degrees C preferably in air and under an oxygen ambient atmosphere in a 700-900-degree C temperature requirement.

The lithium and copper multiple oxide said by this invention are multiple oxides which consist of a lithium and copper as a main constituent, and other elements may be added in the range to which essential structure is not changed.

If the example of a lithium and a copper multiple oxide is shown as an example, LiCuO , Li_2CuO_2 , and Li_3CuO_3 grade are mentioned, and this multiple oxide can be obtained by mixing lithium compounds, such as a lithium carbonate, a lithium hydroxide, and lithium oxide, copper compounds, such as copper carbonate, copper oxide, and copper hydroxide, etc., and calcinating preferably 450 degrees C - 1,200 degrees C in a 600 degrees C - 1,000 degrees C temperature requirement under the conditions of oxygen ambient atmosphere middle arbitration among air.

Although especially the rate of a compounding ratio of $\text{Li}_x\text{MyN}_z\text{O}_2$, and this lithium and copper multiple oxide that is the main active material here is not restricted, if an overdischarge property and discharge capacity are taken into consideration, it is desirable that a lithium and a copper multiple oxide are below 40 weight sections more than 1 weight section to the $\text{Li}_x\text{MyN}_z\text{O}_2$ 100 weight section. Furthermore, they are below 20 weight sections more than 5 weight sections more preferably below 25 weight sections more than 5 weight sections.

Although it is not yet clear about the mechanism of action of this lithium and copper multiple oxide, this compound itself has the lithium ion emission capacity which was excellent at the time of an initial charge. If the example of Li_2CuO_2 shows concretely



***** has occurred electrochemically, and although the lithium ion burst size changes with conditions, the value of w reaches the value of 0.8-1.2 by charge with the potential of 4.2V to a lithium. In the characteristic thing, this lithium and copper multiple oxide by which the initial charge was carried out, namely, DIN TAKARESHON was carried out are not ***** (ing) discharge capacity and discharge potential. That is, it is imagined as what is working only as a source of supply of a lithium ion at the time of an initial charge.

Also when the positive-electrode main active material and positive-electrode secondary active material based on a presentation of this invention are used based on this property and it is set to 0V at the time of overdischarge, i.e., cell voltage, for the aforementioned reason, although negative-electrode potential changes with conditions, it is held in the range which is 1.5V-3.5V, and an overdischarge property is improved remarkably.

Although especially the negative-electrode active material used by this invention is not limited, carbonaceous ingredients, such as conductive polymer negative electrodes, such as polyacetylene and Poly p-phenylene, pitch system carbon, and a vapor growth carbon fiber, etc. are mentioned.

The effectiveness which was excellent when the matter which can intercalate lithium

ions, such as a carbonaceous ingredient, like the above was used for a negative electrode is demonstrated.

The electrode using the active material of said this invention as a basic component in the case of assembling the nonaqueous rechargeable battery of this invention and also a separator, and nonaqueous electrolyte are mentioned. Although are not limited especially as a separator, and textile fabrics, a nonwoven fabric, a glass cloth, the synthetic-resin fine porosity film, etc. are mentioned, when using a thin film and a large area electrode like the above-mentioned, the synthetic-resin fine porosity film indicated by JP,58-59072,A, especially the polyolefine system fine porosity film are desirable in respect of thickness, reinforcement, and membrane resistance.

Although not limited especially as an electrolyte of nonaqueous electrolyte, if an example is shown, LiClO_4 , LiBF_4 , LiAsF_6 , $\text{CF}_3\text{SO}_3\text{Li}$, LiPF_6 , LiI , LiAlCl_4 , NaClO_4 , NaBF_4 and NaI , 4 (n-Bu) N^{+}ClO_4 , 4 (n-Bu) N^{+}BF_4 , and KPF6 grade will be mentioned.

Moreover, as an organic solvent of the electrolytic solution used, although ether, ketones, lactone, nitril, amines, amides, a sulfur compound, chlorinated hydrocarbons, ester, carbonate, a nitro compound, a phosphoric ester system compound, a sulfolane system compound, etc. can be used, for example, ether, ketones, nitril, chlorinated hydrocarbons, carbonate, and a sulfolane system compound are desirable also among these.

Furthermore, it is annular carbonate preferably.

As these examples of representation, a tetrahydrofuran, 2-methyl tetrahydrofuran, 1,4-dioxane, an anisole, mono-glyme, an acetonitrile, Propionitrile, 4-methyl-2-pentanone, butyronitrile, Valeronitrile, a benzonitrile, 1,2-dichloroethane, gamma-butyrolactone, Dimethoxyethane, a methyl FORU mate, propylene carbonate, Although ethylene carbonate, vinylene carbonate, dimethylformamide, dimethyl sulfoxide, a dimethyl thio formamide, a sulfolane, a 3-methyl-sulfolane, trimethyl phosphate, phosphoric-acid triethyl, these mixed solvents, etc. can be raised It is not necessarily limited to these.

Furthermore, if it requires, a cell is constituted using components, such as a charge collector, a terminal, and an electric insulating plate. Moreover, especially as structure of a cell, although not limited, if it requires further, the gestalt of a positive electrode, a negative electrode, the paper mold cell that used the separator as the monolayer or the double layer when requiring further, a laminating mold cell or a positive electrode, a negative electrode, the cylindrical cell around which the separator was wound in the shape of a roll will be mentioned as an example.

[Effect of the Invention]

The overdischarge property which was the fault of the conventional nonaqueous cell is improved by leaps and bounds, and the cell of this invention has it as noncommercial uses, such as an object for small electronic equipment, and an object for electric vehicles, and an industrial power source. [very useful]

[Example]

Hereafter, an example and the example of a comparison explain this invention in more detail.

Example of manufacture of a lithium and a copper multiple oxide After mixing the 2nd copper of oxidation with a lithium carbonate by the mole ratio of 2:1, Li_2CuO_2 was obtained by calcinating at 940 degrees C in air for 18 hours.

The ball mill ground this Li_2CuO_2 in mean particle diameter of 15micro, and it used for the following examples and the example of a comparison.

Example 1 Use LiCoO_2 as positive active material, and Li_2CuO_2 is used as a positive-electrode secondary active material. Make graphite and acetylene black into an electric conduction agent, and a fluororubber is used as a binder. What was respectively mixed by the weight ratio of LiCoO_2 : Li_2CuO_2 :graphite:acetylene black:fluororubber =100:12:7.5:2.5:2 is considered as a dimethyl amide paste. Use as a positive electrode the sheet which carried out spreading desiccation at aluminum foil, and needle coke powder is used as a negative-electrode active material. The fluororubber was used as the binder, by considering as a dimethylformamide paste what was mixed by the weight ratio of needle coke:fluororubber =95:5, the sheet which carried out spreading desiccation was used as the negative electrode at nickel foil, Li metal was made into the reference pole, and the cell shown in [Fig. 1](#) was manufactured.

In addition, the polypropylene nonwoven fabric was used as a separator 3, and the liquid which adjusted hoe lithium fluoride to the concentration of 1.0M was used for the mixed solvent (volume ratio = 1:1) of propylene carbonate and a butyrolactone as the electrolytic solution.

After charging this cell by constant-voltage 4.2V for 5 hours, it discharged on termination electrical-potential-difference 2.7V conditions by the constant current of 1.0 mA/cm².

After repeating this charge-and-discharge cycle 5 times, the overdischarge shelf test was performed. Namely, the forward negative terminal was left for one week in the state of the short circuit through 5-ohm resistance. The charge-and-discharge cycle in the account condition of Gokami was repeated 5 times. Change of the discharge capacity at this time is shown in [Fig. 2](#) , and the electrical-potential-difference change at the time of

overdischarge is shown in [Fig. 3](#) . As for negative-electrode potential, 2.2V were shown, when the cel electrical potential difference was set to 0V so that clearly from [Fig. 3](#) . The fall of the capacity by this overdischarge test is not seen at all so that clearly from [Fig. 2](#) .

Example 1 of a comparison Used LiCoO_2 as the positive-electrode main active material, made graphite and acetylene black into the electric conduction agent, used the fluororubber as the binder, and the sheet which carried out spreading desiccation was used as the positive electrode at aluminum foil by considering as a dimethylformamide paste what was respectively mixed by the weight ratio of LiCoO_2 :graphite:acetylene black:fluororubber =100:7.5:2.5:2, and also the same cell as an example 1 was manufactured, and same evaluation was performed. A result is shown in the 1st table, [Fig. 4](#) , and [Fig. 5](#) .

When the cel electrical potential difference was set to 0V at the time of overdischarge so that clearly from [Fig. 5](#) , negative-electrode potential was rising to 3.9V. Moreover, capacity was falling sharply by this overdischarge test so that clearly from [Fig. 4](#) .

Examples 2-11 Same actuation was completely performed except having changed as the compounding ratio of LiCoO_2 and Li_2CuO_2 was shown in the 1st table in the example 1. A result is combined and is shown in the 1st table.

第 1 表

※1

	配合比 (重量ベース) $\text{LiCoO}_2:\text{Li}_2\text{CuO}_2$	過放電時の 負極電位 (V)	容 量 mAh/gr	過放電後の 容量低下 (%)
比較例1	100:0	3.90	149	15.3
実施例2	100:3	3.80	147	8.5
実施例3	100:5	3.71	148	5.3
実施例4	100:8	2.74	146	0
実施例5	100:11	2.20	144	0
実施例6	100:14	2.08	140	0
実施例7	100:17	2.06	103	1.5
実施例8	100:20	2.05	91	1.1
実施例9	100:30	2.02	60	0.8
実施例10	100:40	2.00	53	0.5
実施例11	100:50	1.86	28	1.4

※1 正極1gr当りの放電容量 (2.7Vcut 時)

Example 12 The completely same actuation was performed except having used $\text{LiCo}_{0.97}\text{Sn}_{0.03}\text{O}_2$ instead of LiCoO_2 in the example 1.

Example 13 The completely same actuation was performed except having used $\text{LiCo}_{0.7}\text{nickel}_{0.3}\text{O}_2$ instead of LiCoO_2 in the example 1.

A result is shown in the 2nd table.

第 2 表

	過放電時の 負極電位 (V)	放電容量 (mAh/正極1gr)	過放電後の 容量低下
実施例 12	2.15	153	0
実施例 13	2.23	123	0

Example 14 The polyacetylene negative electrode was used as a negative electrode, and also the completely same actuation as an example 1 was performed. The method of preparation of a polyacetylene negative electrode is as follows.

Toluene 50ml was taken to the glassware of 800ml of content volume under N₂ ambient atmosphere, tetrabutoxytitanium 6ml and triethylaluminum 10ml were added, and the catalyst was prepared. The inside of a system after cooling a container at -78 degrees C was exhausted, catalyst liquid was applied to the container wall surface, and acetylene gas was introduced. Film-like polyacetylene generated on the wall surface immediately, and the inside of an after [15 minute neglect] system was exhausted. After after [washing] 0.5N-HCl-MeOH washed 5 times with toluene, it dried and took out.

It used, after heat-treating this film-like polyacetylene for 5 seconds at 250 degrees C. A result is shown in the 3rd table.

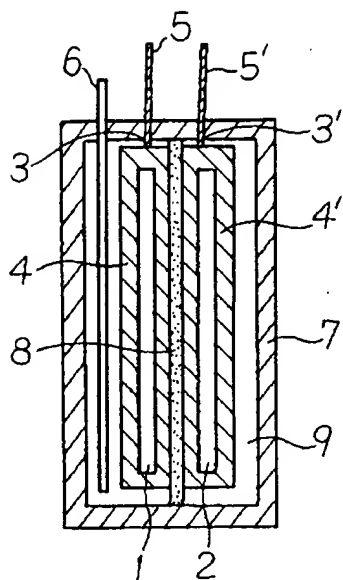
Example 2 of a comparison The polyacetylene negative electrode was used as a negative electrode, and also the completely same actuation as the example 1 of a comparison was performed.

A result is shown in the 3rd table.

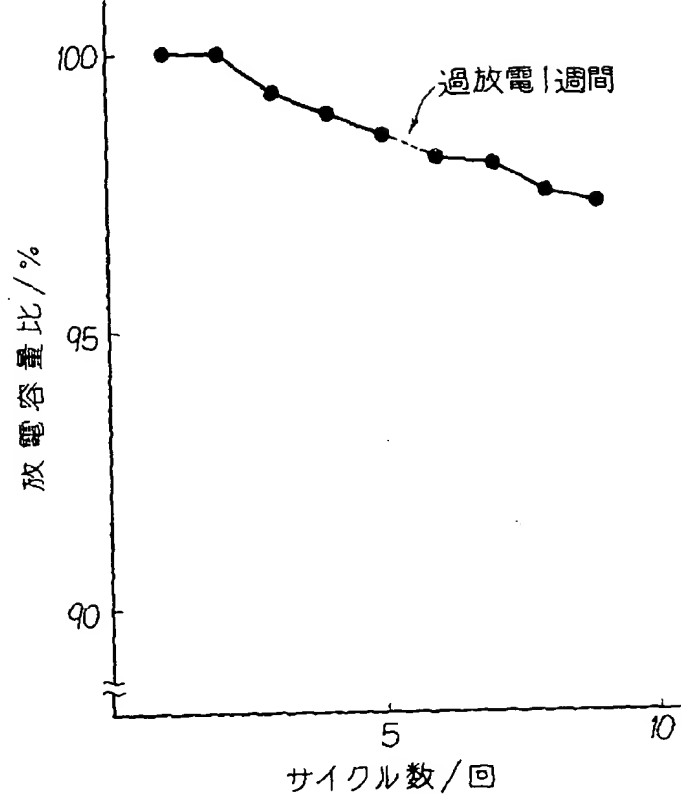
第 3 表

	過放電時の 負極電位 (V)	放電容量 (mAh/正極1gr)	過放電後の 容量低下 (%)
実施例 13	2.16	148	0
比較例 3	3.82	141	10.4

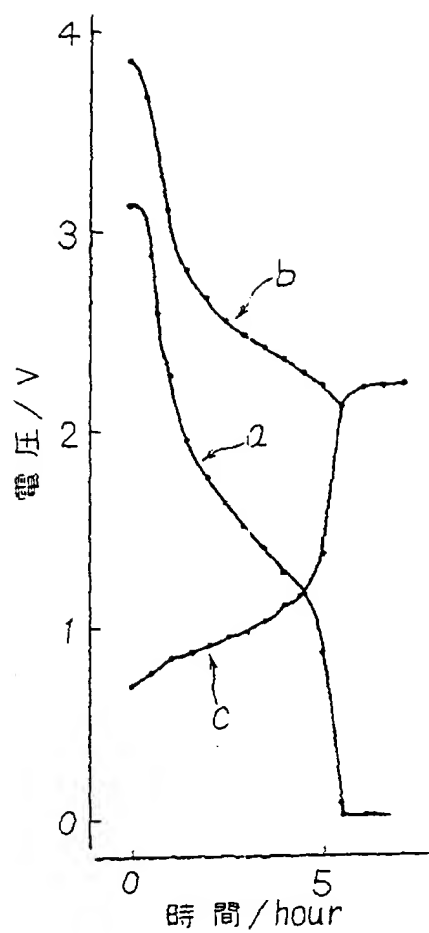
Drawing 1



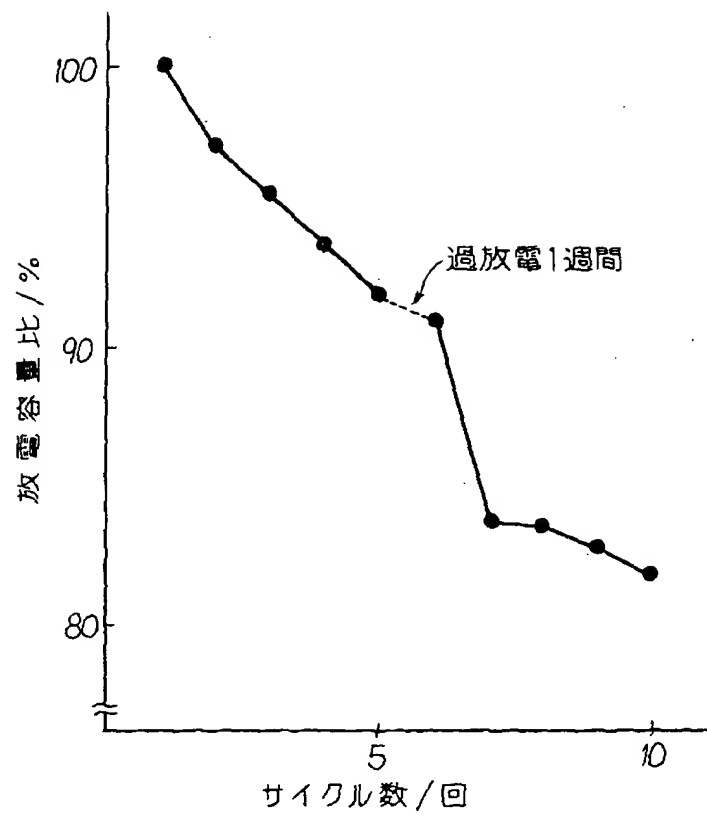
Drawing 2



Drawing 3



Drawing 4



Drawing 5

